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Barks as biosorbent for exclusion of heavy metals-A review

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ABSTRACT

Heavy metals are non-biodegradable and tend to accumulate in living organisms causing diseases and disorders. Conventional methods for their removal are often ineffective (especially at environmental levels), expensive and unavailable in developing countries. Biosorption is an emerging field in removal of heavy metals for its cost effectiveness, selectivity, high efficiency, minimization of chemical and /or biological sludge, no additional nutrient requirements, and regeneration of biosorbent with possibility of metal recovery. It has great potentials for application in developing economies especially in India because of available profuse biodiversity as it involves the use of living or non-living biological materials for pollutants' removal from aqueous solutions and industrial effluents. Present paper has elucidated developments in the use of barks as biosorbents for the remediation of waters and wastewater as an upcoming green technology with practical futuristic relevance.

Keywords: Biosorption, Heavy metals.

INTRODUCTION

The increased use of heavy metals in process industries such as the electroplating, tanning and textile industries, also use of insecticides, pesticides and fertilizers often results in the generation of large quantities of dilute effluents containing mixtures of heavy metals, posing environmental disposal problems. In addition, mining, mineral processing and extractive metallurgical operations produce large amounts of metal bearing liquid wastes requiring treatment. Unlike most other toxic pollutants, metals can accumulate throughout the food chain due to their non biodegradability and thus have potentially detrimental effects on all living species. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested beyond the permitted concentration, they can cause serious health disorders [1]. Arsenic, cadmium, chromium, copper, lead, mercury, zinc are chief examples of heavy metals having potential health effects on long term exposure like skin damage, kidney damage, allergic dermatitis, Wilson's disease, high blood pressure, delayed physical and mental development and even cancer. Heavy metals are common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel etc, as listed in table I.

Table I: Heavy metals in industrial applications

Industries	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Ti	Zn
General Industry and Mining			√	√	√		√		√		√
Plating		√	√	√				√	√		√
Paint Products			√						√	√	
Fertilizers		√	√	√	√	√	√	√	√		√
Insecticides / Pesticides	√			√		√					
Tanning	√		√								
Paper Products			√	√		√		√	√	√	√
Printing / Dyeing			√						√		

Many conventional methods like chemical precipitation, coagulation, ion exchange, electro-chemical methods, membrane separation, oxidation, are available for the treatment of heavy metals. Major disadvantages of these methods are high sludge production, handling and disposal problems, high cost, and technical constraints. Thus there is a continuing interest in the development of more cost-effective and environmentally-benign processes of selective removal of heavy metals from dilute wastewater streams. Adsorption technique can has been proved to be an excellent method to treat industrial waste effluents, offering significant advantages like low-cost, availability, profitability, easy operation and efficiency [2]. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. In recent years, various natural have been tried to achieve effective removal of various heavy metals. Biosorption is a form of adsorption process involving the removal of metal ions from a liquid phase onto a solid biomass material. Some biosorbents are expected to be competitive with existing non-biomass based treatments [3].

Techniques for Treatment of Heavy Metals : There are many chemical, physical and biological technologies available for the removal of metal ions from effluents which have been traditionally employed for heavy metal removal from industrial wastewater [4]. However, the shortcomings of most of these methods are of high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment. A combination of different processes is often used to achieve the desired water quality in the most economical way [5]. Chemical methods entail coagulation together with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation process by oxidizing agents, irradiation and electro chemical processes. Even though these methods are efficient for treatment of water contaminated with pollutants, they are pricey and commercially unattractive. Also towering electrical energy requirement and use of chemical reagents is a general problem.

Physical methods include membrane filtration and adsorption. Membrane filtration procedures are ion exchange, nano filtration, reverse osmosis and electro dialysis. The major drawbacks of membrane filtration are high expenditure, lesser number of metal ions removal and limited lifetime. Adsorption is one of the most accepted ways of pollutant removal from effluents, given that proper design of the process furnishes good effiency for treating effluents. Adsorption provides prominent alternative for treatment of contaminated water, in particular if the adsorbent is low-cost and does not necessitate any additional pretreatment step before use.

Biological methods such as Phytoremediation involve the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantages include that it takes a long time for removal of metals and the regeneration of the plant for further biosorption is difficult also biological methods require large area and are constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation [6, 7]. Incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents. Comparison of various technologies is listed in table 2.

Table 2: Comparison between various technologies for heavy metal removal

Method	Advantage	Disadvantage
Chemical Coagulation	▪ Dewatering ▪ Sludge settling	▪ High cost ▪ Large consumption of chemicals
Chemical Precipitation	▪ Simple ▪ Inexpensive ▪ Most metals can be removed	▪ Large amount of sludge production ▪ Disposal problem
Electrochemical methods	▪ Metal selective ▪ Pure metals can be achieved	▪ High capital cost ▪ High running cost
Membrane Filtration	▪ Metal selective ▪ High regeneration of materials	▪ High cost ▪ Less number of metal ions removed
Adsorption Using Activated Carbon	▪ High efficiency (99%) ▪ Most metals can be removed	▪ Cost of activated carbon ▪ Performance depends upon adsorbent

Compared to other techniques for removal of heavy metals, adsorption is found to be superior in terms of outlay, simplicity of design, ease of operation, litheness, minimization of chemical and/or biological sludge also it does not lead to formation of unsafe substances [8].

Adsorption: Adsorption is a separation process, of attracting and retaining the molecules of a substance at the surface a solid or a fluid resulting into higher concentration of the molecules on the surface than in the bulk. The phenomenon of the enrichment of chemical substances at the surface is called ‘adsorption’. All adsorption performance processes are depends on solid-liquid equilibria and on mass transfer rates [9]. If the mass transfer is in opposite direction then it is called as ‘Desorption’. Adsorption is one of the promising processes for the removal of heavy metals from water. The process is suitable even when the metal ions are present in concentration as low as 1mg L^{-1} [10].

Types of Adsorption

At molecular level, adsorption is due to attractive interactions involving a surface and the species being adsorbed.

Physical adsorption: It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.

Chemical adsorption: It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. It is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorptions considered like chemical reaction. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisoption often involves large activation energy (Activated adsorption).

Application of Adsorption: Adsorption can be applied to both gaseous and liquid separations.

Gaseous separations:
1. Removal of toxic gases and removal of objectionable odors from industrial gases for air pollution control and deodorization of air.
2. Recovery of valuable solvents vapors from dilute mixtures of air or other gases.
3. Fractionation of mixtures of hydrocarbon gases.

Liquid separations:
1. Removal of moisture dissolved in gasoline.
2. Decolourization of petroleum products and aqueous sugar solutions.
3. Removal objectionable taste and odor from water.
4. Fractionating mixtures of aromatic and paraffin hydrocarbons.

- In the electrochemistry, molecules adsorbed to the surface of an electrode donate or accept electrons from the electrode.
- Adsorption plays an important role in processes such as heterogeneous catalysis.
- Purification by adsorption is perhaps the oldest known application. Wine clarification is still accomplished by the use of adsorbents. Exhausts of industrial plants can be stripped off undesired components.

Adsorbents: Adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. Separation occurs because of differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The overall rate of adsorption is controlled by the rate of diffusion of solute within the capillary pores of the adsorbent and varies with square root of the contact time with the adsorbent. A fundamentally important characteristic of good adsorbents [11, 12] is their high porosity and consequent larger surface area with more specific adsorption sites. Most adsorbents which have been used in pollution control have porous structure. The porous structure not only increases surface area and consequently adsorption but also the kinetics of the adsorption. A better adsorbent is the one with large surface area and which requires less time for adsorption equilibrium. The adsorption operation can be batch, semi-batch and continuous. Batch operations are generally conducted when small amounts are to be treated. The equilibrium distribution depends on the contact time in batch operation [13]. Some widely used conventional adsorbents for pollution management and different industrial procedures are as discussed.

Silica gel: Silica gel is the most widely used desiccant (adsorbent for moisture) because of its large adsorption capacity for water (~ 40% by weight). This quality is due to its relatively weak bonds with water as well as larger pore volume and mesoporosity [14]. Further, ease in regeneration (~ 150°C) makes silica gel most widely used desiccant. The gel is considered a good adsorbent and is used in any industries for drying of gases and liquids, purification of hydrocarbons etc [15, 16].

Zeolites and ion exchange resins: Zeolites are alumino silicates with Si/Al ratios between 1 and infinity. There are 40 natural and over 100 synthetic zeolites. They are also considered as selective adsorbents. Zeolites generally show a surface area [17] in the range of 1-20 m^2/g. Zeolite based materials are used in detergent manufacture, ion-exchange resins (i.e. water softeners), catalytic applications in the petroleum industry, separation process (i.e. molecular sieves) and as an adsorbent for water, carbon dioxide and hydrogen sulphide. Various zeolites have been employed for the removal of water pollutants by various researchers e.g. for the removal of methylene blue dye from water [18], for the removal of phenols and chlorophenols [19] and for the removal of and methylisoborneol from drinking water [20]. A number of ion-exchange resins have also been used for the removal of specific organic compounds. Weak and strong acid-type resins used for removal of cations are called cation exchangers whereas base-type resins that remove anions are called anion exchangers. The primary applications of ion-exchange resins are the softening and deionization of water. Other applications are waste treatment, catalysis, purification of chemicals and pharmaceutical. Recently, anion-exchange resins have been used for the removal of dyes [21].

Activated carbon is a form of carbon species that is processed and prepared to have high porosity and very large surface area available for adsorption. Activated carbons are sometimes called as active carbons due to their highly developed internal surface area and porosity. The large surface area implies a high capacity for adsorbing chemicals from gases and liquids. The most widely used commercial active carbons have a specific surface area varying from 800 to1500 m^2 g^{-1}, as determined typically by nitrogen gas adsorption (BET surface area) [22]. Difference in pore size affects the adsorption capacity for molecules of different shapes and sizes, and thus is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes. They are:
Micropores: width less than 2 nm
Mesopores: width between 2 nm and 50 nm
Macropores: width greater than 50 nm
However, the activated carbon used in wastewater treatment is generally prepared from coconut shells, peat, sawdust, wood char, bio-wastes (**Kaza's Carbons**), lignin, petroleum coke, bone char, anthracite coal etc [23].

Preparation of Activated Carbon: Activated carbon is generally produced from carbonaceous materials or in general biomass substances like nutshells, peat, wood, bagasse, lemon peels, lignite and coal etc. It can be produced by one of the following processes.

Physical activation: The precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes:

- *Carbonization*: Material with carbon content (the biomass precursor) is pyrolyzed at high temperatures, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)
- *Activation/Oxidation*: Raw material (precursor) or carbonized material (product obtained from carbonization) is exposed to oxidizing agents (carbon dioxide, oxygen, or steam) at high pressure and temperature[22].

Chemical activation: The raw material is impregnated with certain chemicals at specific ratios before carbonization. The chemical is typically an acid, strong base, or a salt (nitric acid, hydrochloric acid, phosphoric acid, potassium hydroxides, sodium hydroxide, zinc chloride, etc. depending on its utilisation). Then, the impregnated raw material is carbonized at lower temperatures (comparatively lower than physical carbonization). It is believed that the carbonization and activation occurs simultaneously during chemical activation. Chemical activation is preferred over physical activation because it requires lower temperatures and shorter time for activating the material [22, 24].

Types of Activated Carbon: Classification is done based upon their surface characteristics, behavior and preparation methods.

Powdered Activated Carbon (PAC): Powdered Activated Carbon is fine granules whose size is less than 1.00 mm. Their average pore diameter is between 0.15 to 0.25 mm. They are usually prepared by finely ground raw material. PAC is not generally used because of their high pressure loss in applications. However, their main property is the presence of a high surface area to volume ratio.

Granular Activated Carbon (GAC): Granular Activated Carbon is comparatively larger in size than Powdered Activated Carbon. This type of activated carbon exhibits a lower surface area than PAC. GAC is used for deodorization, water treatment and separation of components in a flow system and can also be used for gas/vapor phase applications.

Extruded activated carbon (EAC): Extruded Activated Carbon is cylindrical shaped activated carbon with diameters ranging from 0.8 to 130 mm. Since they are of bigger size they have high mechanical strength, low dust content and low pressure drop during application. Hence they are used for gas phase applications.

Impregnated carbons: Inorganic metals like aluminum, manganese, zinc iron, lithium and calcium are impregnated upon them for specific applications related to air pollution control. This type of activated carbon also finds usage in water purification processes when impregnated with specific kinds of antimicrobial/antiseptic agents.

Polymers coated carbon: It is a process of preparing biocompatible polymer to give a smooth and permeable coat without blocking the pores. It is used as an absorbent in hemoperfusion and other medical related adsorption operations.

Pellet Activated Carbon: Pellet Activated Carbon is generally used where high pressure operations and high volumetric adsorption is required. As the name suggests, these activated structures are compact, hard and have a very high surface area for adsorption. Usually pellet activated carbons have a length of 20 mm to 40 mm and a diameter of 5 to 10 mm. The main reason to use a pellet for adsorption is because of its unique pore distribution. The mesoporosity of these pellets are highly enhanced and hence have a great effect in gas adsorption processes. However, due to certain fluctuations in production, these pellets can also be used for liquid adsorption purposes too [25]. The main application and function of an activated carbon is determined by its characteristic studies like BET surface area, SEM, FTIR, Iodine Number, Carbon Tetrachloride Number, etc.

The major applications of Pellet Activated Carbon are [25]:

1. Solvent Recovery
2. Gas purification and processing
3. Volatile Organic Compounds Control
4. Catalyst Support
5. HVAC (Heating, Ventilation and Air Conditioning)

Commercial activated carbon is a preferred adsorbent for the removal of micro pollutants from the aqueous phase. Research and experiments are done to find inexpensive alternative activated carbon (AC) precursors, such as waste materials. It is evident that conventional (from agriculture and wood industry) and nonconventional (from municipal and industrial activities) wastes can be used to prepare AC, which are applied in treatment processes, namely to remove organic pollutants, dyes, volatile organic compounds, and heavy metals from water and other liquid medium. Moreover, high surface areas can be obtained using either physical or chemical activation. But combined treatments might enhance the surface properties of the activated carbon having higher adsorption capacity [26].

Biosorption: Biosorption is a property of certain types of inactive, dead, microbial biomass, biological material to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. The term, biosorption is thus used to describe the passive non-metabolically mediated process of metal binding to living or dead biomass [27]. Biosorption of heavy metals from aqueous solutions can be considered as an alternative technology in industrial wastewater treatment. The technique is an emerging technology based on the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or physico – chemical pathways of uptake [28]. The major advantages of biosorption over conventional treatment methods include [29]:

- Low cost;
- High efficiency;
- Minimisation of chemical and /*or* biological sludge;
- No additional nutrient requirement;
- Regeneration of biosorbent; and
- Possibility of metal recovery.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

Biosorbents: A variety of low-cost biomass has been developed and commercialized for controlling pollution from diverse sources in different parts of the world [30]. They include anaerobically digested sludge [31], bacteria [32], fungi [33] and algae [34]. Agricultural materials have also been used. These include rice bran, soybean and cottonseed hulls [35], crop milling waste [36], maize cob meal [37], coir, jute and sawdust [38], canola meal [39] and coconut shell [40] amongst others. Biosorption uses inexpensive dry biomass to extract toxic heavy metals from industrial effluents. The biomass can be shredded or ground to yield stable biosorbent particles. Alternatively, it can be immobilized by a synthetic polymer or fixed onto an inorganic support material. The biosorbent particles can be packed in columns which are the most effective devices for continuous removal of heavy metals. Once the metal binding reaches saturation, the biomass can be regenerated with acid and/or hydroxide solutions, which discharge small volumes of concentrated heavy metal. The advantages of biosorption are low operating costs, minimal volumes of chemical disposal and/or biological sludge and high efficiency in detoxifying very dilute effluents. These advantages constitute the primary incentives for developing full-scale biosorption processes for the removal of heavy metals from contaminated solutions [41]. The use of dead biomass is of particular economic interest, because the biomaterials are used the same way as synthetic adsorbents or ion exchangers and repeated regeneration is possible [42]. Biosorption has been found to be a more rapid mechanism; hence, it has a more significant role in metal sorption from wastewater. Biological treatment processes for removing heavy metals from wastewater are most effective when contaminant concentrations are below and above 100 mg L^{-1} [43].

Mechanism of Interactions with Metal Species : The mechanism of biosorption is complex, mainly ion exchange, chelation, adsorption by physical forces, entrapment in inters and intra-fibrilliar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes. There are several chemical groups that would attract and sequester the metals in biomass: acetamido groups of chitin, structural polysaccharides of fungi, amino and phosphate groups in nucleic acids, amido, amino, sulphhydryl and carboxyl groups in proteins, hydroxyls in polysaccharide and mainly carboxyls and sulphates in polysaccharides of marine algae that belong to the divisions Phaeophyta, Rhodophyta and Chlorophyta. However, it does not necessarily mean that the presence of some functional group guarantees biosorption, perhaps due to steric, conformational or other barriers.

Choice of Metal for Biosorption Process : The appropriate selection of metals for biosorption studies is dependent on the angle of interest and the impact of different metals, on the basis of which they would be divided into four major categories: (i) toxic heavy metals (ii) strategic metals (iii) precious metals and (iv) radio nuclides. In terms of environmental threats, it is mainly categories (i) and (iv) that are of interest for removal from the environment and/or from point source effluent discharges. Apart from toxicological criteria, the interest in specific metals may also be based on how representative their behavior may be in terms of eventual generalization of results of studying their biosorbent uptake. The toxicity and interesting solution chemistry of elements such as chromium, arsenic and selenium make them interesting to study. Strategic and precious metals though not environmentally threatening are important from their recovery point of view.

Choice of Sorbent for Biosorption Process : Almost any biomass derived product can be used for metal ion removal from solution. In principle, transportation cost and associated usage of energy can be minimized by using locally collected biomass as the basis for biosorbent system. But the overall cost and energy expenditure will also depend on the performance of the material. One needs to consider that a higher-performing biosorbent may achieve one’s objectives for metal removal with much less biosorbent material, thus reducing labor costs and operational costs. There may be saving related to safe disposal or regeneration of the spent material. The ideal biosorbent should be very cheap, an unwanted byproduct that currently has to be hauled away and land filled or burnt in heaps. On the other hand, the ideal biosorbent should have a huge appetite for a broad range of metal ions, binding them quickly, tightly, and dependably. One approach is just to test various readily available materials in “as-received” form. However, as will be shown in the course of this review, other investigators have employed a more proactive option, treating the biomass in various ways to improve its performance.

Cost : The word “low cost” have been used frequently, especially in review articles, by authors summarizing the main motivations promoting the use of biosorbent technology. the operating costs involved in the usage of biosorbents for metal removal can be low relative to various alternative pollution abatement measures, there has been insufficient attention to operating cost, including the cost of transporting the sorbent material to the point of use, as well as costs associated with transportation to a site of final disposal, regeneration, or other beneficial use [44].

Local availability of large quantities : One promising low transportation cost strategy is to position one's bioremediation facility adjacent to a business that produces suitable lignocellulosic waste stream. For example substantial quantities of microbial biomass are produced during industrial scale fermentation processes [45]. Likewise, there may be opportunities to accumulate such byproduct as bark, sawdust, or ash adjacent to a facility that produces wood products or paper pulp as a primary product.

Modification of Biosorbents : Once a decision has been made to use a certain type of biosorbent, perhaps due to favorable performance of the as-received material, the next decision may involve whether and how to modify that material to improve its efficiency, this is achieved by various methods like:

Size reduction : In principle, a more finely ground sample of a given cellulose-based material is expected to adsorb more metal ions from solution, under specified conditions, compared to coarser particles. Indeed, this statement has been proven in a few studies [46]. A further question is whether the effort and expense of size reduction can be justified. A study observed an increase in metal sorption capacity by only a factor of about 2 when the particle size of sawdust was decreased from 500 µm to 100 µm [47]. In addition to high energy requirements, especially if one aims to achieve particles much smaller than 1 mm, one can anticipate increased problems with the handling of very fine material, including greater difficulties in later separation from the water phase, clogging of filters, and even dust and fire hazards if and when the material is dried. Sawdust actually represents a favorable case, since the energy to reduce the particle size has already been expanded, perhaps in the production of lumber. Unfortunately, there have been few studies dealing systematically to determine under what circumstances one can justify the energy and time needed to reduce the particle size of a selected biomass sample in preparation for its use as a metal sorbent.

Heat Treatment : Drying of biomass also has been reported by many researchers as having a positive effect on metal uptake [48]. However, there has been almost no systematic study of this important issue.

Alkaline Treatment : Treatment with alkaline solution has been shown to enhance metal uptake in a few cases [49, 50]. The mechanism has not been confirmed in detail. It seems likely that saponification of various ester groups may be involved, increasing the number of carboxylate groups on the treated surfaces [51].

Oxidation : One kind of treatment that has been consistently shown to increase the ability of cellulose-derived substrates to adsorb cationic metal species is oxidation [52]. As already has been noted, oxidation of cellulose-derived material may result in increased numbers of carboxyl groups, which can be dissociate to their negatively charged carboxylate form as the pH is increased in a range of 3 to 6.

Chemical Derivatisation : Chemical derivatisation of cellulosic material can be defined as the covalent attachment of various functional groups. This approach makes it possible for technologists to select chemical functionalities that may be expected to enhance metal uptake. From a scientific standpoint, derivatisation also can be considered as a way to evaluate different hypotheses regarding which chemical groups, some of which may be present naturally, are likely to contribute to observed metal binding effects.

Carboxylic acid derivatives : Earlier it was noted that carboxylic acid groups contribute directly to the ion exchange capacity of sorbent materials. Accordingly, many authors have reports favorable effects on metal uptake when using biosorbents that have been derivatized to increase their carboxylic acid content. In general, such approaches have been shown to increase the adsorption capacity of a biosorbent for the target metals.

Multifunctional carboxylic acid derivatives : Esterification of a cellulose-based polymer with 1,2,3-propanetricarboxylic acid was fund to yield strong binding as a wide range of heavy metals [53]. By such a reaction, there is potential to create adjacent carboxylic acid sites at the sorbent surface. Ideally, if one were to use just the right monomer, there is a theoretical possibility to approach the strong metal binding capabilities of a chelating agent. However, one needs to keep in mind that the most effective chelating agents require three to six carboxylic acid groups in a specific arrangement that is best suited for coordinating with a given type of metal ion [54].

Pyrolizing to Produce Activated Carbon Products : Very strong heating in the relative absence of oxygen is known to convert cellulosic materials into carbon. Careful control of the pyrolysis conditions, including the temperature and the composition of the surrounding gases, make it possible to achieve a very high accessible surface area per unit mass, in addition to providing significant control regarding the chemical sites at the carbon surface [55]. For instance, the pore structure often can be enhanced by the use of steam during preparation of the activated carbon [56]. Numerous strategies have been used to render activated carbon products more effective in the uptake of one or more kinds of metal ions. In general, these modifications can be achieved by the following strategies: First, the gaseous conditions can be adjusted, e.g. by the addition of steam, controlled amounts of oxygen, and by controlling the temperature, etc. Second, the mixture fed into the pyrolysis chamber can be treated, for instance, with such materials like phosphoric acid to achieve a higher proportion of carboxylic acid groups or phosphorous-containing groups on the resulting carbon surface. Finally, the resulting powder can be post-treated, e.g. with nitric acid, to oxidize the surface, thus increasing the number of carboxyl groups [57].

Barks as Biosobents : Large amounts of bark residues are generated annually by timber processing mills worldwide. Bark residues are one of the most abundant renewable resources that are available for conversion into high value, environmentally sustainable biomaterials, including low cost sorbents for treatment of contaminated water streams. The volume of bark residue is so great that it must be continually removed from mill sites. Utilization of bark is receiving increasing attention as it is a useful byproducts waiting for the right economic conditions or the development of satisfactory commercial processes. Air pollution regulations and high stumpage prices make maximum utilization of forest products a must. Efficient bark utilization can create a new industry and boost the economy by making a valuable asset out of a costly waste. It is significant that many major wood processing companies are currently investing huge sums in the construction of bark processing plants. Bark comprises the outer part of woody stems and branches. Anatomically it includes all the plant tissues outside the cambium. Although the term “bast” is sometimes used as the equivalent of bark, or inner bark, it applies more correctly only to the lignified fibers commonly found in many barks and other fibrous plant materials. These may amount to 35-45 percent of some inner barks. Bark formation is initiated by the process of cell division at the cambium, which produces xylem on the woody side (inside) and phloem, the primary bark tissue, on the exterior bark side. Phloem tissue contains phloem parenchyma, bast fibers, companion cells, and the very important sieve cells or sieve tubes. The sieve elements are the main channel for downward movement of sap and nutrients from the leaves contra to the upward rise of water from the roots in the xylem. The layer of physiologically active tissue adjacent to the cambium is known as the inner bark and is generally relatively thin and light colored. As subsequent layers of phloem are laid down year by year, the outer layers become crushed and compressed, and the sieve elements and similar structures collapse. This tissue then ceases to take part in active physiological processes and is transformed into the relatively inert, dark outer bark that comprises the bulk of most tree barks. The rifted or scaly outermost layer of such bark on mature trees is then called the rhytidome. The structure of bark is further complicated by the presence of a second cambial layer within the bark called the phellogen or cork cambium. Periderm, or cork, is produced by this cork cambium and contributes appreciably to the structure of the outer bark. The innermost layer of periderm is normally considered as the boundary between the inner and outer bark. A number of other types of auxiliary tissues, e.g. lignified sclerynchyma and medullary ray parenchyma, are also found in bark. This brief description indicates that bark is a highly complex, heterogeneous material composed mainly of a thin, physiologically active inner layer and a complex, relatively inert outer layer, whose principal functions are to protect the cambium and prevent loss of water.

In keeping with its heterogeneous structure, the chemical composition of bark exhibits great diversity, so that analytical data on bark samples are difficult to obtain and are often not very meaningful. Vast differences in the nature and amounts of various chemical components and of various extraneous materials contained within the bark can be found within even a single species, depending on the age and growth site of the trees sampled and the fraction of bark examined, etc. Differences in composition and variation in amounts of common constituents can, of course, be much larger between species and, for these reasons; there are no good standardized methods of bark analysis. Bark flour is effective for removal of toxic heavy metal ions from water because of its high content of polyhydroxy polyphenolic groups that are capable of chelating heavy metal ions. The polyhydroxy polyphenol groups of tannin are thought the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate [58]. In addition, bark contains carboxylic groups, which can bind metals by ion exchange mechanism. However, because bark also contains significant quantities of water soluble extractives, including soluble tannins, which can be detrimental to aquatic life, the bark needs to be treated before it is used as a sorbent material for removal of contaminants from water. Earlier studies indicated that water soluble phenolic substances in bark can be condensed into water insoluble polymers by high temperature heating. Table III shows some of the tree barks used as adsorbents in removal of heavy metals from water with their respective adsorption capacities.

Table 3. Tree barks as adsorbents

Adsorbent	Metal ions	Adsorption capacity (mg/g)	References
Acacia Nilotica Bark	Cr(VI)		[59]
Black oak bark	Cd	25.9	[60]
	Hg	400	
	Pb	153.3	
Cassava tuber bark waste	Cd(II),		[61]
	Cu(II),		
	Zn(II)		
Cassava tuber bark waste	Cd (II)	45.61	[62]
	Cu(II)	54.21	
	Zn(II)	28.95	
Cassia siamea bark	Cd (II)	9.81	[63]
Douglas fir bark	Hg	100	[60]
Eucalyptus bark	Cu(II)	0.45	[64]
	Pb(II)	0.55	[64]
Eucalyptus bark	Zn (II)	1.68	[65]
Eucalyptus bark	Cd (II)	14.53	[66]
Eucalyptus bark and Cassia fistula bark	Cr, Cu		[67]
Eucalyptus bark	Cr	45	[68]
Hemidesmus indicus bark	Pb(II)		[69]
Hardwickia binata bark	Cd	34	[70]
Mango bark saw dust	Zn (II)	1.028	[65]
Moringa oleifera bark	Ni(II)	30.38	[71]
Rhizophora apiculata mangrove bark	Ni(II)	7.25	[72]
Rhizophora apiculata mangrove bark	Cu(II)	6.95	[72]
Neem bark	Cr (VI)	19.60	[73]
Pine bark	Cd (II)	7.50	[74]
Pinus pinaster bark	Cd (II)	8.00	[75]
Pinus pinaster bark	Cd (II)	8.0	[76]
Pinus ponderosa bark	Cu (II)	57	[77]
	Zn (II)	53	
	Cd (II)	50	
	N i(II)	27	
Pinus roxburghii bark	Cr(VI)	4.15	[78]
	Zn(II)	3.89	
	Cu(II)	3.81	
	Ni(II)	3.53	
	Cd(II)	3.01	
Pinus sylvestris bark	Cr (III)	9.77	[79]
Redwood bark	Cd	27.6	[80]

Metal biosorption by biomass mainly depend on the components on the cell, especially through cell surface and the spatial structure of the cell wall. Some functional groups have been found to bind metal ions, especially carboxyl group. There is some evidence to confirm that the O-, N-, S-, or P-containing groups participate directly in binding a certain metals. Some active sites involved in the metal uptake are determined by using techniques of titration, infra-red and Raman spectroscopy, electron dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electron microscopy (scanning and/or transmission), nuclear magnetic resonance (NMR), X-ray diffraction analysis (XRD), XAFS (X-ray absorption fine structure spectroscopy) etc.

CONCLUSIONS

Biosorption has advantages compared with conventional techniques some of which include:

- Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.
- Metal selective: the metal sorbing performance of different types of biomass can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.
- Regenerative: biosorbents can be reused, after the metal is recycled.
- No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.
- Metal recovery possible: In case of metals, it can be recovered after being sorbed from the solution.
- Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor.

Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria and plant materials etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption.

Biosorption by barks have various advantages, and hence are increasingly being used as biosorbents specifically in India the relevance is wider because of profuse available biodiversity. Biosorption as a technology has wide scope for tapping its advantage as an eco friendly method of metal remediation.

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